Magnetic Behaviour of Perovskite Compositions Derived from BiFeO₃

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Abstract: The phase content and sequence, the crystal structure, and the magnetic properties of perovskite solid solutions of the \((1-y)\)BiFeO₃\(-y\)BiZn\(_{0.5}\)Ti\(_{0.5}\)O\(_3\) series (0.05 ≤ \(y\) ≤ 0.90) synthesized under high pressure have been studied. Two perovskite phases, namely the rhombohedral R\(3c\) and the tetragonal P\(4mm\), which correspond to the structural types of the end members, BiFeO₃ and BiZn\(_{0.5}\)Ti\(_{0.5}\)O\(_3\), respectively, were revealed in the as-synthesized samples. The rhombohedral and the tetragonal phases were found to coexist in the compositional range of 0.30 ≤ \(y\) ≤ 0.90. Magnetic properties of the BiFe\(_{1-y}\)[Zn\(_{0.5}\)Ti\(_{0.5}\)]O\(_3\) ceramics with \(y < 0.30\) were measured as a function of temperature. The obtained compositional variations of the normalized unit-cell volume and the Néel temperature of the BiFe\(_{1-y}\)[Zn\(_{0.5}\)Ti\(_{0.5}\)]O\(_3\) perovskites in the range of their rhombohedral phase were compared with the respective dependences for the BiFe\(_{1-y}\)Bi\(_{3+}\) O\(_3\) perovskites (where Bi\(_{3+}\) = Ga, Co, Mn, Cr, and Sc). The role of the high-pressure synthesis in the formation of the antiferromagnetic states different from the modulated cycloidal one characteristic of the parent BiFeO₃ is discussed.

Keywords: atomic substitution; Néel temperature; G-type antiferromagnetic; weak ferromagnetism; collinear magnetic ground state

1. Introduction

Bismuth ferrite is one of few type-I multiferroics, namely those solids in which the coexisting (anti)ferroelectric order and the (anti)ferromagnetic order are caused by independent mechanisms [1]. Ferroelectricity in BiFeO₃ is induced by the electronic instability of the lone-pair Bi\(_{3+}\) cations, while the antiferromagnetism in this material with the Néel temperature, \(T_N\), as high as 643 K results from the superexchange interactions between Fe\(_{3+}\) cations [2]. Besides, the distorted crystal structure of this perovskite, involving large polar atomic displacements and octahedral tilting, gives rise to competing antisymmetric Dzyaloshinskii-Moriya (DM) interactions [3]. The part of antisymmetric exchange associated with the polar distortions favours a spatially modulated ground state in the form of a long-period incommensurate cycloid. Contrary, the antisymmetric exchange imposed by the octahedral tilting requires a non-modulated canted weak ferromagnetic (FM) state. In
the undoped BiFeO₃, the former contribution wins promoting the long-period modulated spin ordering that averages the net magnetization to zero [4]. This modulation, however, can be suppressed via chemical modification or thin-film strain engineering, resulting in a state where both the ferroelectric polarization and spontaneous magnetization coexist.

The bismuth site substitutions in BiFeO₃ are the most studied. The compositional dependent structural transitions and variations of the magnetic ordering of the Bi₁₋ₓAₓFeO₃ perovskites series (0 ≤ x < 1) have been revealed [5–8]. In particular, the minimum substitution rates for rare earth cations sufficient to destroy the cycloidal modulation were estimated [9]. Besides, the correlations between the size of the substituting cation and the transition temperature were found [5,10].

Chemical modifications in the iron site of BiFeO₃ appear to be the direct approach to tune the magnetic behaviour of this material. However, using the conventional synthesis routes, it is possible to achieve the substitution rates of a few at.% only. Most of the reported single-phase BiFe₁₋ₓBₓFeO₃ perovskite compositions with x > 0.10 were prepared using the high-pressure synthesis technique [11–21]. The only exception appears to be the BiFe₁₋ₓMnₓO₃ system, in which up to about 30 at.% of the iron-to-manganese substitution is possible via the conventional ceramic route [22]. It should be noticed here that the B-site substituted compositions derived from bismuth ferrite using the conventional route belong to the same space group, R3c, as that of the parent BiFeO₃, while high-pressure synthesis can result in the formation of other structural phases. For instance, the same perovskite composition, BiFe₀.₇₅Mn₀.₂₅O₃, prepared by solid-state synthesis at ambient pressure or via high-pressure synthesis is rhombohedral or orthorhombic, respectively [22]. The full-range range substitutions of Fe³⁺ with trivalent cations whose ionic radii are considerably smaller (gallium [16]) or considerably larger (scandium [19]) than the iron one were successfully performed using high-pressure synthesis. In high-pressure stabilized perovskite solid solutions of the BiFe₁₋ₓScₓO₃ system a series of structural transitions with increasing y was found. Moreover, it was revealed that annealing the as-prepared BiFe₁₋ₓScₓO₃ perovskites (y ≥ 0.3) results in irreversible transformations into new perovskite phases with interesting combinations of ferroic orders [23]. It was demonstrated that the observed effect is a manifestation of conversion polymorphism, which is a general phenomenon in the high-pressure stabilized oxygen-octahedral structural phases [23]. Structure, dielectric response, and magnetic behaviour of the as-prepared and the converted polymorphs of the (1-y)BiFeO₃-yBiScO₃ perovskites have been considered in great detail [24–27]. Magnetic ordering was detected in the BiFe₁₋ₓScₓO₃ compositions with up to 60 at.% of scandium with a near-linear T₅(N/2) dependence. In the 0.1 ≤ y < 0.3 range of this solid solution system, some peculiarities of the temperature-dependent magnetic moment below T₅(N) were observed and associated with possible transitions between three different antiferromagnetic (AFM) structures, namely those corresponding to collinear, canted, and cycloidal spin arrangements [26]. Similar temperature anomalies of the magnetic behaviour below T₅(N) were then revealed in the Fe-rich compositional range of the BiFe₁₋ₓ[Zn₀.₅T₁₀.₅]₀.₅O₃ perovskites phases prepared using high-pressure synthesis [28]. The (1-y)BiFeO₃–yBiZn₀.₅T₁₀.₅O₃ series is of interest as the promising lead-free system in which the compositional range of coexistence of two polar phases (the morphotropic phase boundary/region, MPB) occurs.

Although a number of the BiFe₁₋ₓBₓO₃ perovskite series has already been prepared and characterized [11–21,28,29], to the best of our knowledge, the obtained structural and magnetic data have not been generalized in respect of the ionic size of the substituting cation. This is certainly worthy of consideration as the comparative studies of the variation of structural characteristics and transition temperatures in solid solutions and series the isomorphous substitutions of are known to be very convenient to understand some features and predict properties of new compositions [30].

In this paper, we considered the compositional behaviours of the crystal structure and the magnetic properties of the BiFe₁₋ₓ[Zn₀.₅T₁₀.₅]₀.₅O₃ perovskite phases and compared them with the respective dependences of BiFe₁₋ₓBₓO₃ perovskites (where B³⁺ = Ga, Co, Mn, Cr, and Sc) in the vicinity of parent bismuth ferrite. Among these, Cr³⁺, Mn³⁺,
and Co$^{3+}$ are magnetic cations of transition metals from the same 3$d$ series to which iron belongs, while Ga$^{3+}$, Sc$^{3+}$ and [Zn$_{0.5}$Ti$_{0.5}$]$^{3+}$ are non-magnetic. Besides, as compared with iron, Ga$^{3+}$ is smaller, Sc$^{3+}$ is considerably bigger, and [Zn$_{0.5}$Ti$_{0.5}$]$^{3+}$ is slightly bigger than Fe$^{3+}$ in octahedral coordination. Although no simple model based on microscopic magneto-structural correlations can be applied and predicting the behaviour of the doped perovskites requires extensive DFT calculations that include detailed information about the structural modifications [7], the compared cases appear to be various enough to conclude on possible correlations and trends.

2. Results

Analysis of the XRD data of the as-synthesized (unannealed) samples of the $(1−y)$BiFeO$_3$–$y$BiZn$_{0.5}$Ti$_{0.5}$O$_3$ series has revealed no crystalline phase apart from the perovskite ones. It was found from the comparison of the XRD patterns of the compositions with increasing $y$ that the samples with $y < 0.30$ are single-phase perovskites with the rhombohedral $R3c$ structure. An increase of the Zn-Ti content results in the appearance and growth of new diffraction peaks (Figure 1). These peaks were associated with the tetragonal perovskite phase similar to that of the parent BiZn$_{0.5}$Ti$_{0.5}$O$_3$ [31]. In the range of $0.30 ≤ y ≤ 0.90$, the rhombohedral and the tetragonal phases coexist. These two were the only phases detected in the whole compositional range, and no other perovskite phase has been revealed. This is in contradiction with the results of Pan et al. [18]) who observed an intermediate monoclinic phase in BiFe$_{1−y}$[Zn$_{0.5}$Ti$_{0.5}$]$_y$O$_3$ between $y = 0.40$ and 0.50. It should be noted, however, that Pan et al. studied the annealed samples while no thermal treatment was performed in this work. As mentioned in the Introduction, annealing of the high-pressure stabilized materials can lead to irreversible polymorph transformations [23].

![Figure 1](image-url)

Figure 1. The XRD patterns of the $(1−y)$BiFeO$_3$–$y$BiZn$_{0.5}$Ti$_{0.5}$O$_3$ samples as-synthesized under high pressure. The numbers at the diffractograms denote the $y$ values. The shadow areas indicate the angular ranges of (001)$_p$, (011)$_p$ and (111)$_p$ reflection families of the primitive perovskite lattice. The dotted lines point out the 2Theta positions of the reflections corresponding to the rhombohedral $R3c$ phase (red lines) and the tetragonal $P4mm$ phase (blue lines).

The compositional range of coexistence of the rhombohedral and the tetragonal structural phases (MPB) in the BiFeO$_3$–BiZn$_{0.5}$Ti$_{0.5}$O$_3$ system is essentially broader than that
observed in the BiMg_{0.5}Ti_{0.5}O_{3}−BiZn_{0.5}Ti_{0.5}O_{3} solid solutions [32], in which the bismuth magnesium titanate is a structural analogue of PbZrO_{3} [33]. In the latter system, a coexistence of the perovskite phases was observed in the compositional range narrower than 5 at.%. A wide-range coexistence of the perovskite phases is very typical of the compositions derived from bismuth ferrite since the energy landscape of BiFeO_{3} is rather flat [34].

The crystal structure refinement was successful considering the two perovskite phases in the as-prepared the BiFe_{1−y}[Zn_{0.5}Ti_{0.5}]_{y}O_{3} samples, namely the rhombohedral R3c and the tetragonal P4mm, which correspond to the structural types of the end members, BiFeO_{3} and BiZn_{0.5}Ti_{0.5}O_{3}, respectively.

The compositional variations of the primitive perovskite unit–cell parameters (a_{p}, c_{p}, and a_{p}) and the normalized unit-cell volume (V_{p} = V/Z) are shown in Figure 2. The parameters were calculated from the refinement data using the relations for the basis vectors of the rhombohedral R3c structure and the parent cubic cell [28]. One can see no significant increment of any of the parameters with y over the whole range. The maximum relative variations were observed for the c_{p} value (~0.6%, the P4mm phase) and the V_{p} value (~1.4%, R3c phase). As a result, the difference between the normalized unit-cell values of the phases is almost constant over their coexistence range (Figure 2b).

![Figure 2](image_url)

**Figure 2.** (a) The primitive perovskite cell parameters and (b) the normalized unit-cell volume of the BiFe_{1−y}[Zn_{0.5}Ti_{0.5}]_{y}O_{3} perovskite phases as a function of y with the ranges of phase coexistence (0.30 ≤ y ≤ 0.90) indicated. The data for the end members (y = 0 and y = 1) were taken from Refs. [31,35], respectively. The polyhedral representations of the respective structures are shown.

The most representative results of magnetic measurements of the BiFe_{1−y}[Zn_{0.5}Ti_{0.5}]_{y}O_{3} samples are shown in Figures 3 and 4. It was earlier found [28] that the Néel temperature is more pronounced in magnetic data for the heat-treated samples. Therefore, the annealed samples were used for the estimation of the T_{N} values. The temperature dependence of the magnetic moment measured in the field-cooled (FC) regime in an applied magnetic field of 500 Oe from the temperature high enough above the transition temperature down to 330 K is shown in Figure 3.
Two anomalies in the temperature-dependent magnetic moment considered as indications of magnetic transformations (assigned as $T_m$ and $T_a$) were observed in the AFM state of the BiFe$_{1-y}$Sc$_y$O$_3$ ceramics in the compositional range of $0.1 \leq y < 0.25$ [26]. The signature of similar behaviour was also observed in the BiFe$_{1-y}$[Zn$_{0.5}$Ti$_{0.5}$]$_y$O$_3$ phase with $y = 0.25$ [28]. Therefore, the low-temperature magnetic moment of BiFe$_{1-y}$[Zn$_{0.5}$Ti$_{0.5}$]$_y$O$_3$ with $0.1 \leq y < 0.2$ was measured in the temperature range of 5–400 K in a small applied field of 50 Oe. Similar behaviour was observed for as-synthesized and annealed samples. As can be seen from the data measured using as-synthesized samples in zero-field-cooled (ZFC) regime in Figure 4, for low $y$ values, there is no clear signature of the transformations as mentioned above in contrast to BiFe$_{1-y}$Sc$_y$O$_3$ [26]. Possible transformations of the magnetic
structure shown by arrows in Figure 4 were revealed for \( y = 0.2 \) only from the derivative of the \( M/H(T) \) curve.

An interesting behaviour was observed in the magnetization loops. The shape of the magnetization loops of the as-synthesized BiFe\(_{1-y}\)[Zn\(_{0.5}\)Ti\(_{0.5}\)]\(_{y}\)O\(_3\) samples resembles those of BiFe\(_{1-y}\)Sc\(_{y}\)O\(_3\) [36], which can be described as a superposition of linear AFM and hysteretic FM contribution. The annealing leads to an increase in coercivity, remnant magnetization, and the total magnetization at the maximum applied field. Example data are depicted for \( y = 0.15 \) in the inset of Figure 5 with \( H_C = 1.43 \) kOe and \( H_C = 4.63 \) kOe for the as-synthesized and the annealed sample, respectively. The observed change in the shape of the magnetization loops after the annealing is of particular interest. The magnetization loops clearly indicate the presence of metamagnetic behaviour particularly pronounced in the compositions with \( y = 0.05 \) and \( y = 0.1 \). Apparently, the magnetic state of the studied samples is nonhomogeneous, and they consist of at least two phases. One of them is weak ferromagnet (i.e., canted antiferromagnet), and another is either a modulated cycloid, similar to the undoped BiFeO\(_3\), or collinear antiferromagnet (no spin canting) as in the ground state of polar BiFeO\(_{0.75}\)Sc\(_{0.25}\)O\(_3\) [23]. The metamagnetic behaviour can be attributed to the latter phase, where the magnetic field switches the spin ordering from the modulated to collinear. The field-induced transition is reversible at room temperature resulting in the unusual shape of the magnetization loops. It has to be pointed out that such transition is also well-known in BiFeO\(_3\) [36,37], however, with the critical field significantly higher than in the present case. The phase fraction of the modulated/collinear metamagnetic phase decreases with \( y \), and it vanishes in the compositions with \( y \geq 0.2 \). These experimental observations can be interpreted as a composition-induced first-order phase transition with an extremely large phase coexisting region. In this scenario, the hysteretic region might also depend on temperature, resulting in a very complex composition-temperature-field phase diagram. On the other hand, the weak ferromagnet phase itself can exhibit metamagnetic re-orientation of the magnetic moments at low magnetic fields, as reported in the case of high-pressure synthesized BiFe\(_{0.75}\)Mn\(_{0.25}\)O\(_3\) [22].

![Figure 5](image-url)  
Figure 5. Magnetization loops of the annealed BiFe\(_{1-y}\)[Zn\(_{0.5}\)Ti\(_{0.5}\)]\(_{y}\)O\(_3\) samples measured at 300 K normalized to the magnetization value \( M_{max} \) at the maximum applied field. The inset shows the magnetization loop for the composition with \( y = 0.15 \) before and after annealing.

3. Discussion

It follows from the available data on the bulk perovskite BiFe\(_{1-y}\)B\(_{3-y}\)O\(_3\) solid solutions that the BiFeO\(_3\)-type rhombohedral phase remains in the compositions with up to about
30 at.% substitution rate regardless of the preparation method. In particular, the R3c range is \( y \leq 0.3 \) for Ga [16], \( y \leq 0.25 \) for Co [14], \( y \leq 0.30 \) for Mn [12], \( y \leq 0.25 \) for Sc [19], and \( y \leq 0.30 \) for Zn\(_{0.5}\)Ti\(_{0.5}\) (see Results). The only known exception is the iron-to-chromium substitution, at which BiFe\(_{0.50}\)Cr\(_{0.50}\)O\(_3\) is still rhombohedral [13,20]. In the cases when the perovskite BiFe\(_{1}\)\(_{−}\)\(_y\)Bi\(_{3}\)\(^{3+}\)O\(_3\) phase is prepared via high-pressure synthesis, annealing may extend (by about 5 at.%\) the compositional range of the rhombohedral structure [22,23].

Figure 6 shows the value of the normalized unit-cell volume for the BiFe\(_{1}\)\(_{−}\)\(_y\)Bi\(_{3}\)\(^{3+}\)O\(_3\) perovskites as a function of \( y \) in the range of their R3c phase. The \( V_p(y) \) dependences in this range are roughly linear with the slopes, which correlate well with the ionic radii of these \( Bi^{3+} \) cations in octahedral coordination.

In the BiFe\(_{1}\)\(_{−}\)\(_y\)Bi\(_{3}\)\(^{3+}\)O\(_3\) systems, in which iron is substituted by Mn, Cr, or Sc, the rhombohedral R3c phase borders with the antipolar orthorhombic \( Pm\alpha\) phase [12,19,20]. When the substituting element is Co or Ga, the R3c phase is followed by the monoclinic \( Cm\) one [14,16]. According to results reported by Pan et al. [18], increasing \( y \) in the annealed \((1−y)BiFeO\(_3\)−yBZN\(_{0.5}\)Ti\(_{0.5}\)O\(_3\) ceramics leads to a crossover from the rhombohedral to the monoclinic \( Cc \) structure, while the data obtained in this work indicate that the next perovskite phase in the ceramics as-synthesized under high-pressure is the tetragonal \( P4mm \).

Generally, the structure sequence (starting from the rhombohedral one at \( y = 0 \)) in the BiFe\(_{1}\)\(_{−}\)\(_y\)Bi\(_{3}\)\(^{3+}\)O\(_3\) perovskites is determined by the structural type of the Bi\(_B^{3+}\)O\(_3\) end member. In particular, in spite of the considerable size difference in the \( B^{3+} \) cations, the as-synthesized metastable perovskites BiMnO\(_3\), BiCrO\(_3\), and BiScO\(_3\) all are monoclinic \( C2/c \) [35]. As a result, the sequence of the structural phases in the BiFeO\(_3\) derived solid solutions with these perovskites is the same, namely \( R3c−Pm\alpha−C2/c \) as \( y \) is increased. Analogously, in the solid solutions with BiCoO\(_3\) and BiZn\(_{0.5}\)Ti\(_{0.5}\)O\(_3\), which are both tetragonal \( P4mm \) [31,38], the sequence is \( R3c−Cm \) (or \( Cc \))−\( P4mm \). The crystal structure of BiGaO\(_3\) is of a pyroxene-type [16]. Therefore, the structure sequence observed in the BiFe\(_{1}\)\(_{−}\)\(_y\)Ga\(_y\)O\(_3\) series is essentially different from the aforementioned ones.
The BiFe$_{1-y}$B$_3^+$yO$_3$ perovskites are all antiferromagnets, at least in the range of the rhombohedral phase. Their $T_N$ values are shown in Figure 7 as functions of the substitution rate. One can see that regardless of the nature of the substituting $B^+$ cation, the Néel temperature decreases with $y$. Moreover, the negative increment, $\Delta T_N/\Delta y$ is roughly the same for the solid solutions, in which $B^3^+ = $ Mn, Cr, Sc, and Zn$_{0.5}$Ti$_{0.5}$ (as obtained in this work from Figure 3). To the best of our knowledge, no data on the $T_N(y)$ dependence has been reported regarding the iron-to-cobalt substitution. Taking into account the $T_N(y)$ behaviour for the systems with manganese and chromium, a possible compositional variation of the Néel temperature for the (1-$y$)$\text{BiFeO}_3$-$y\text{BiCoO}_3$ system has been suggested (dashed line in Figure 7). Surprisingly, in the case of the iron-to-scandium substitution [26], magnetic ordering still remains at $y = 0.60$.

![Figure 7](image.png)

**Figure 7.** The Néel temperature as a function of $y$ for the BiFe$_{1-y}$B$_3^+$yO$_3$ perovskites with $B^3^+ = $ Co [39], Mn [12], Cr [29], Sc [26] and Zn$_{0.5}$Ti$_{0.5}$ (this work). A suggested $T_N(y)$ behaviour for the (1-$y$)$\text{BiFeO}_3$-$y\text{BiCoO}_3$ perovskites is shown with the dashed line.

In the annealed samples of the BiFe$_{1-y}$Sc$_y$O$_3$ series with $y = 0.30$, a reversible transition between the AFM state with the cycloidal incommensurate modulation and the collinear AFM ground state was observed at $T_m = 230$ K [23]. The as-synthesized BiFe$_{0.70}$Sc$_{0.30}$O$_3$ phase is the orthorhombic $Pnma$, while the annealed polymorph of this composition is the rhombohedral $R3c$. No such AFM-AFM transition has been detected in the as-prepared material [23]. That is why it was suggested that conversion polymorphism is responsible for the formation of the collinear AFM ground state in BiFe$_{0.7}$Sc$_{0.3}$O$_3$. However, Rusakov et al. [21] have reported on the reversible transition between the AFM states with the cycloidal and the collinear spin arrangements in the high-pressure stabilized BiFe$_{0.8}$Cr$_{0.2}$O$_3$ at $T_m = 260$ K. This composition demonstrates no conversion polymorphism and is rhombohedral before and after annealing. Therefore, the formation of the AFM states different from the modulated cycloidal one can be rather associated with the features caused by the high-pressure synthesis of the aforementioned perovskites.

In addition to the transition at $T_m$, the magnetic measurements of the BiFe$_{1-y}$Sc$_y$O$_3$ samples with compositions 0.10 $\leq y \leq 0.30$ revealed some anomalies in the $M(T)$ dependences at $T_a$ ($T_m < T_a < T_N$) that were also associated with the transitions between different AFM states [26]. As seen from Figure 4, no clear evidence of the AFM-AFM phase transformation (at $T_m$ and/or $T_a$) in BiFe$_{1-y}$[Zn$_{0.5}$Ti$_{0.5}$]$_y$O$_3$ can be found for the compositions with $y < 0.20$, which may point to the differences in the lattice distortions induced by the
substituting atoms of different sizes. Relatively large scandium (with the C.N. 6 ionic radius of 0.89 Å versus 0.69 Å for iron) may cause significant destruction of cycloidal spin arrangement in the parent BiFeO$_3$ at much lower substitution levels as for B$^{3+}$ = Cr and Zn$_{0.5}$Ti$_{0.5}$ that are similar in size to Fe$^{3+}$.

A substitution usually induces short-range (deformation of Fe$^{3+}$ coordination octahedra) and long-range structural distortions with the Fe$^{3+}$–O$^{2−}$–Fe$^{3+}$ bond angle change. This may lead to the change in magnetic exchange and the spin canting due to the induced DM interaction, thus enhancing the FM component of the magnetization [10,40,41], as seen in Figure 5. On the other hand, the bismuth site substitution can also cause FM contribution originating from the created oxygen vacancies due to charge compensation achieved by oxygen deficiency after introducing alkali earth ions (e.g., Ca$^{2+}$) in the BiFeO$_3$ crystal structure [42]. An enhancement of ferromagnetism in BiFeO$_3$ can also be achieved by reducing crystallite size into the nanometre scale when the size becomes comparable with the AFM cycloid period of ~62 nm [43,44]. However, the FM contribution may be enhanced by mechanically induced distortions even in larger BiFeO$_3$ crystallites [45] (as revealed from significant hysteresis in the magnetization loops similar to those shown in Figure 5) when the material is prepared using the mecanochemical synthesis. Such an observation would point to the critical role of the high-pressure synthesis procedure of BiFe$_1$$_{1−y}$B$^{3+}$$_y$O$_3$ perovskite solid solutions introducing mechanical strain and affecting the magnitude of uncompensated magnetic moments in initial cycloidal AFM arrangement. The enhancement of the ferromagnetism and possible spin canting, suggested from the observed shape of the hysteresis loops in Figure 5, may not be solely the result of chemically induced distortions of the iron substitution but a combined effect.

The dependence of the Néel temperature on the B$^{3+}$ substitution rate in BiFe$_{1−y}$B$^{3+}$$_y$O$_3$ perovskites shown in Figure 7 obviously follows the same trend for different types of iron substitution. Present results also suggest that the phenomenon of reversible transitions between magnetic states with different types of AFM ordering (collinear, canted, and cycloidal spin arrangements) shares the same features and deserves a particular study. It is very likely that this phenomenon is rather general and was overlooked in the systems with B$^{3+}$ = Co and Ga.

4. Materials and Methods

Ceramics of the BiFe$_{1−y}$[Zn$_{0.5}$Ti$_{0.5}$]$_y$O$_3$ series (0.05 ≤ $y$ ≤ 0.90) were synthesized under high pressure from the precursors prepared via a solid-state reaction from the stoichiometric oxide mixtures. Details of the precursor preparation and the high-pressure synthesis can be found in Ref. [28].

Phase analysis of the samples before and after annealing was performed using a PANalytical X’Pert Powder X-ray diffractometer (XRD, Ni-filtered Cu Kα radiation) at room temperature. Before the XRD measurements, the samples were reduced into powders. The crystal structure and the magnetic structure of the samples were refined using the FULLPROF package [46].

Magnetic properties of the ceramic samples were measured in the range of 5–300 K using a commercial Quantum Design MPMS3 magnetometer in applied fields up to 70 kOe in both ZFC and FC regimes. For the ZFC measurements, the samples were heated to 400 K, demagnetized from the applied field of 10 kOe to zero field in the Oscillate Mode, and the residual field was removed by the built-in Magnet Reset quench procedure. High temperature (over the range of 300–800 K) measurements were done using a commercial Quantum Design MPMS-XL5 magnetometer equipped with an oven insert. Some of the ceramic samples were annealed prior to the magnetic measurements. Annealings were done in air at 720 K for 1 h.

5. Conclusions

In the as-synthesized (unannealed) ceramics of the BiFe$_{1−y}$[Zn$_{0.5}$Ti$_{0.5}$]$_y$O$_3$ series (0.05 ≤ $y$ ≤ 0.90) prepared using high-pressure synthesis, two perovskite crystalline phases
were detected, namely the rhombohedral R3c, which is similar to that in the parent BiFeO$_3$, and the tetragonal P4mm as that in the high-pressure stabilized BiZr$_{0.5}$Ti$_{0.5}$O$_3$. No other crystalline phases have been revealed in the obtained samples. The rhombohedral and the tetragonal phases coexist in a wide compositional range (morphotropic phase region) of 0.30 ≤ y ≤ 0.90. In this region, the relative difference between the normalized unit-cell values (V$_p$) of the phases is almost constant, ΔV$_p$/V$_p$ ≈ 7%.

The magnetic behaviour of the BiFe$_{1−y}$Zr$_{0.5}$Ti$_{0.5}$O$_3$ solid solutions with y < 0.30 is typical of antiferromagnets whose Néel temperature (T$_N$) linearly decreases with y. Ferromagnetic contribution to their magnetic moment was revealed. This contribution was found to be more substantial in the annealed samples.

The $V_p(y)$ dependences of the BiFe$_{1−y}$Zr$_{0.5}$Ti$_{0.5}$O$_3$ perovskites ($B^{3+}$ = Ga, Co, Mn, Cr, Sc, and Zr$_{0.5}$Ti$_{0.5}$) in the compositional range of their rhombohedral phase are approximately linear with the slopes, which correlate well with the ionic radii of these $B^{3+}$ cations in octahedral coordination. In particular, the biggest positive slope and the biggest negative slope are observed in the series with $B^{3+}$ = Co and Sc, respectively.

In contrast to the $B^{3+}$ ionic size dependent $V_p(y)$ behaviours of the BiFe$_{1−y}$Zr$_{0.5}$Ti$_{0.5}$O$_3$ perovskites, the compositional dependences of the Néel temperature in the range of their rhombohedral crystalline phases are essentially similar regardless of the nature (magnetic or non-magnetic) of the $B^{3+}$ cation.

The anomalies in the temperature behaviour of the magnetic moment below T$_N$ observed in the BiFe$_{1−y}$Zr$_{0.5}$Ti$_{0.5}$O$_3$ perovskites with $B^{3+}$ = Cr, Sc, and Zr$_{0.5}$Ti$_{0.5}$ are assumed to indicate to the reversible transitions between magnetic states with different types of antiferromagnetic ordering (collinear, canted, and cycloidal spin arrangements). Occurrence of such transitions is likely to be characteristic of the high-pressure stabilized nature of the BiFe$_{1−y}$Zr$_{0.5}$Ti$_{0.5}$O$_3$ perovskites and deserves a particular study.

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